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Chemical Speciation and Health Risk Assessment of Heavy Metals in Urban and Agricultural Soil - A Review

Suneet Kumar Sahni
Assistant Professor
Department of Chemistry
Government (P.G.) College, Bisalpur Pilibhit

Abstract
Heavy metal contamination of urban and agricultural soils creates two distinct threats to human health worldwide. The standard methods used to assess environmental conditions through total metal concentration measurements lead to incorrect danger assessments because they fail to consider how elements distribute themselves geochemically. This paper evaluates the transition towards chemical speciation through BCR and Tessier sequential extraction methods which enable researchers to separate labile components from dissolved materials. The study assesses how urban road dust exhibits technogenic alkalinity while agricultural areas experience bioavailability decreases due to acidification which results from soil chemistry changes that influence metal movement. The USEPA Human Health Risk Assessment model shows that Hazard Quotients and Carcinogenic Risks become more accurate when bioavailable fractions serve as the basis for assessment. The review establishes that adaptive mitigation methods including biochar application and Phyto stabilization need to function as essential tools for managing soil-to-human exposure pathways which will change because of climate alterations.

Keywords: Heavy Metal Contamination, Concentration Measurements, Chemical Speciation, USEPA Human Health Risk Assessment, Phyto Stabilization etc.

I. Introduction:

The Evolving Paradigm of Soil Contamination

The persistent and non-biodegradable characteristics of Lead (Pb), Cadmium (Cd), Arsenic (As), and Mercury (Hg), coupled with their protracted impacts on biological entities, render these elements a significant environmental hazard. Historically, "total metal concentration" has functioned as the primary criterion for evaluating soil quality within environmental monitoring and regulatory frameworks [1]. This methodology establishes a baseline for elemental load, which researchers utilize to evaluate risks to both environmental and human health, notwithstanding its acknowledged limitations as an assessment tool. The total concentration approach assumes that each milligram of a metal in the soil is equally mobile and toxic. This view, however, ignores the complex biogeochemical interactions that affect how these elements behave in real-world situations.

The Constraints of Total Concentration Metrics

The total concentration method suffers from its main weakness because it fails to consider bioavailability which refers to the fraction of metal that living organisms can absorb. Soil exists as a diverse system that includes mineral components and organic materials and pore water which interact with heavy metals through various chemical bonding methods. The soil sample shows high chromium content; however, the metal exists inside the mineral's permanent silicate structure which results in low danger for both groundwater and plant uptake [2]. The total metal concentration in a system shows lower toxicity when the metal exists in a highly soluble and exchangeable form. The existing mismatch between two elements requires scientists to concentrate their studies on chemical speciation which identifies all existing forms of elements in their physical and chemical characteristics. Without this distinction cleanup operations will incorrectly target permanent sites while they should find dangerous areas with low metal contamination that can move through the environment [3].

Extent of Heavy Metal Contamination in Contemporary Environments

Heavy metal pollution reaches different levels according to various land use patterns which create separate pollution patterns for both urban and rural areas. The primary sources of pollutants in urban areas result from "technogenic" activities which include vehicle emissions and tire degradation that produces Zinc and the remains of lead-based paint and industrial smelting operations [4]. The human population living in densely populated areas faces direct health hazards because these metals accumulate in topsoils and road dust. The agricultural practice of using phosphate fertilizers which contain trace amounts of cadmium together with past applications of arsenical pesticides leads to agricultural soil contamination. The rural areas spread danger through their food system which allows metals to move from soil into edible parts of crops and cause lasting dietary exposure. The establishment of health risk assessments that extend beyond basic concentration mapping needs researchers to comprehend these particular pathways which show how metals move and how they poison.

Chemical Speciation:

Frameworks and Methodological Approaches

Chemical speciation denotes the allocation of an element across specific chemical species or categories within a system. The soil science field uses the term "fractionation" to describe the process which separates metals into distinct geochemical phases based on their bonding strength and solubility characteristics. The shift from total concentration to speciation is crucial because different chemical forms of metals lead to distinct patterns of environmental movement and biological absorption and toxic effects on living organisms [5]. The water-soluble and exchangeable metal fractions provide plants with easy access to metal uptake which also leads to metal leaching into groundwater while the silicate mineral lattice trapped metals in the residual fraction maintain geochemical stability and present minimal to no immediate environmental threat.

The BCR and Tessier Extraction Protocols

The most precise method for determining these fractions requires the use of successive extraction methods. Tessier method (1979) established a system for metal classification which categorizes metals into five distinct groups: exchangeable metals, carbonate-bound metals, iron-and-manganese-oxide-bound metals, organic-bound metals, and residual metals. The researchers published extensive work about the Tessier method but the method faced criticism because its chemical components exhibit selective characteristics [6]. The European Community Bureau of Reference (BCR) developed a standardized three-step process which includes a fourth testing step that has become the global standard for examining soil samples.

The BCR process begins with an analysis of materials that can be dissolved in weak acids and materials that can be exchanged. The process requires the application of acetic acid which releases metals that were previously bound to clay and carbonate materials. The most hazardous component of the metal load exists in this particular section. The "reducible" fraction is separated in the second step by using hydroxylamine hydrochloride. The process involves metals which are contained within iron (Fe) and manganese (Mn) oxide minerals. The metals become released when the earth experiences oxygen depletion which can occur during flooding events [7]. The third step uses hydrogen peroxide and ammonium acetate to extract the oxidizable portion. This process enables the extraction of metals found in organic materials and sulphides. The experts can detect the residual fraction after they dissolve the mineral components using aqua regia or powerful acids.

Bioavailability and Environmental Vulnerability

Scientists use these fractions to calculate the "Risk Assessment Code" (RAC) which measures the metal content present in both exchangeable and carbonate fractions. The soil reaches "very high risk" status for nearby environments when labile metal content exceeds 50 percent regardless of total metal concentration. The chemical difference between two substances gains importance for scientists who study environmental transformations resulting from acid rain and fluctuating water table levels. The process of soil pH decline causes metals to leave their carbonate-bound state and enter soil solution which shifts a "latent" pollutant into an "active" toxin state [8].

Analytical Difficulties in Speciation

Chemical speciation through successive extraction methods shows practical value yet has fundamental limitations. The process requires substantial work because it depends on the assumption that all soil chemical reagents will only react with specific soil components which rarely happens with complex soil material. The sample treatment process which includes drying and grinding procedures leads to unintentional changes in metal oxidation states for metals like Chromium and Arsenic which results in incorrect assessment of their actual in-situ speciation. The combination of X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) with traditional wet chemistry methods enables researchers to study metal bonding at the molecular level while maintaining the integrity of soil structure [9].

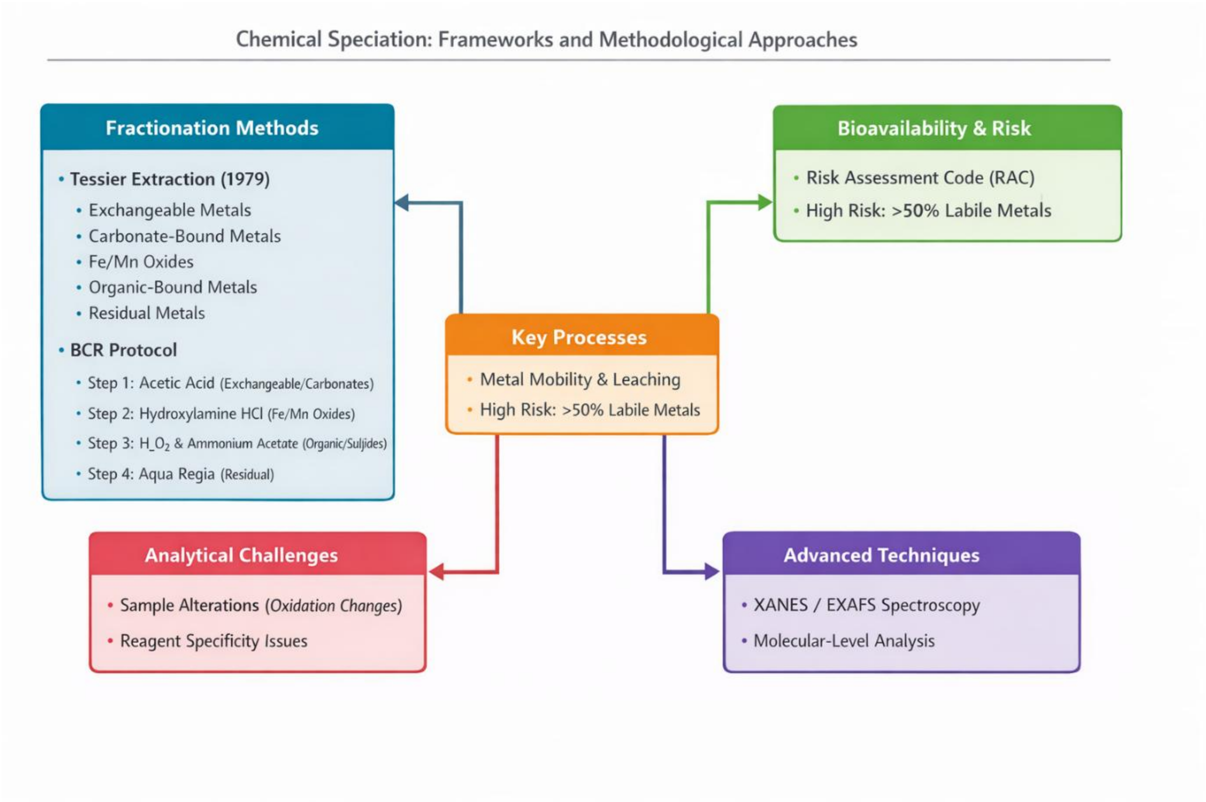

Figure 1: Chemical speciation overview and methods, Source: Author Generated

Comparative Dynamics:
Urban versus Agricultural Soil Environments

The geochemical behavior and toxicological characteristics of heavy metals depend on two main factors which include the historical land use of an area and the soil matrix's physical and chemical characteristics. Urban and agricultural soils function as storage sites for human-made contaminants yet the two ecosystems show significant differences in which contaminants enter their systems and how they become chemically stable. Urban areas experience two main types of pollution which include localized "technogenic" pollution and agricultural areas face "diffuse" pollution that spreads widely through controlled chemical use. The process of human exposure assessment needs these distinctions for accurate modeling while efficient remediation work depends on the same information.

Urban Soils: The Heritage of Industry and Infrastructure

The soils in urban areas display multiple distinct types of soil which contain human-made materials that include construction waste and ashes and asphalt. The soils in these areas show higher pH values because concrete and cement materials release calcium carbonate through leaching processes. The elevated pH level functions as a stabilizing factor which causes Lead (Pb) and Copper (Cu) to become immobilized through their conversion into hydroxide or carbonate forms [10]. Urban areas experience their most significant danger from direct physical contact with substances instead of people consuming plants. Full traffic flow creates two effects because it causes tire wear to release Zinc (Zn) and brake linings to discharge Cadmium (Cd) which both settle as fine particles on soil surfaces. The high population density in cities leads to children in recreational areas who breathe contaminated road dust and dirt becoming the main group that gets exposed to danger. The urban heat island effect accelerates the breakdown process of human-made materials which results in the potential release of metals that remained contained within secure urban building materials.

Agricultural Soils: The Chemically Intensive Paradigm

Soils used for farming operations possess unique chemical properties which determine their nutrient dynamics through two primary factors: soil acidity and nutrient cycling. The extensive application of nitrogen-based fertilizers results in soil pH reduction which increases the solubility and bioavailability of heavy metals [11]. The main challenge in these conditions is the transfer of metals from the soil solution into the tissues of food crops. Cadmium serves as a major pollutant in this context because it exists as a trace contaminant in phosphate fertilizers which leafy vegetables and cereal grains easily absorb through their root systems. Cadmium and Arsenic from agricultural activities can move through the soil profile to reach groundwater sources or build up in the parts of plants that people eat. This establishes a persistent exposure route for people via the consumption of contaminated food which makes the "soil-to-crop" transfer factor more important than direct soil ingestion for agricultural risk assessments.

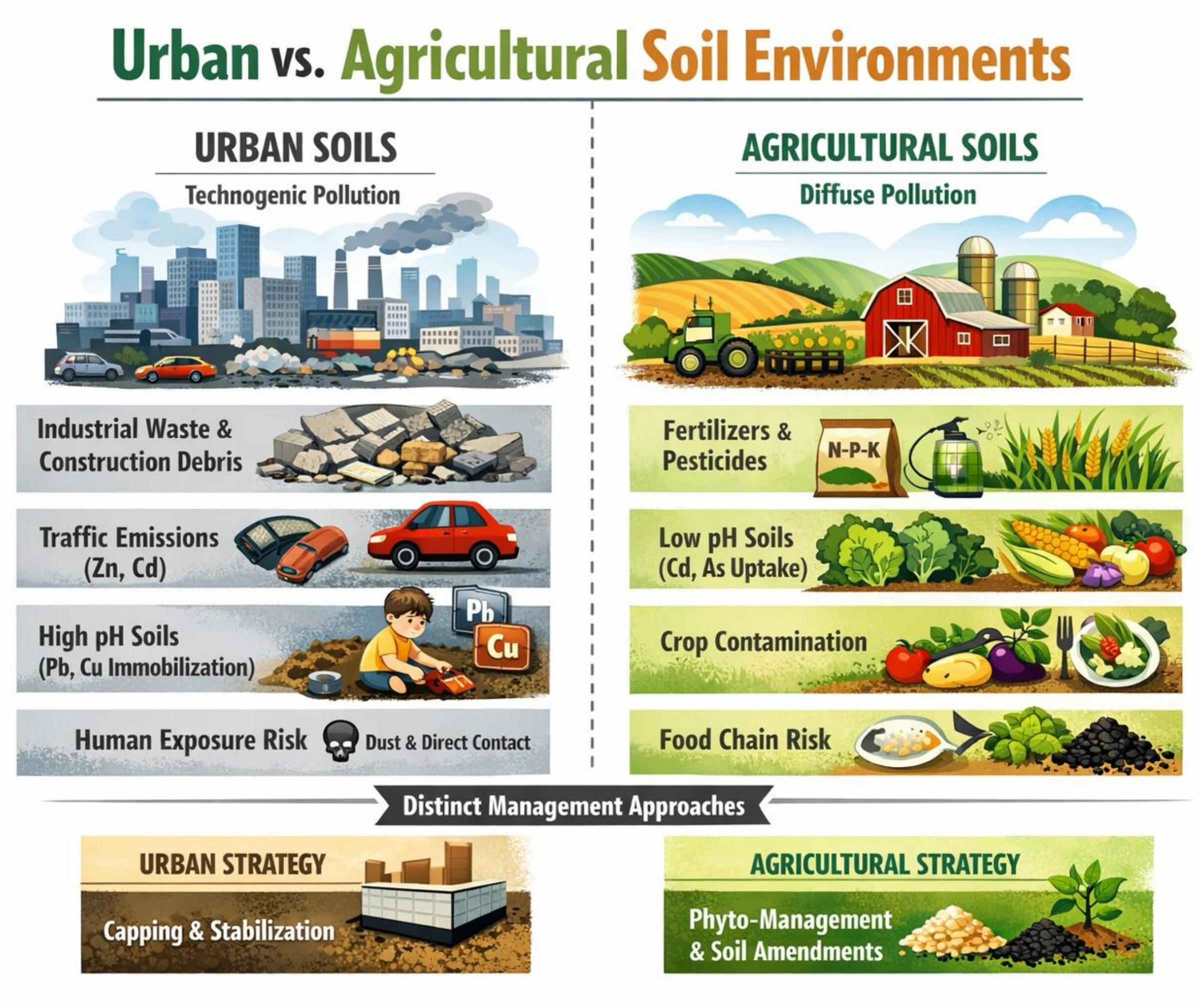

Figure 2: Urban and agricultural soil contrasts, Source: Author Generated

Synergistic Risks and Management Considerations

The two contexts present different situations which need separate management methods to handle their respective requirements. In urban environments, remediation typically emphasizes "capping" or physical stabilization methods to control dust emissions and prevent direct contact with hazardous materials. In agricultural regions the process shifts to "phyto-management," which uses soil amendments that include charcoal and lime to increase pH levels while the amendments work to bind metals in non-labile forms which restrict crop uptake. The organic matter present in agricultural soils which researchers' study under controlled conditions acts as a dual-purpose material because it binds with metals like copper through complexation and it enables metals to travel through the soil as soluble organo-metallic complexes [12]. Heavy metal assessment requires multiple approaches because different environmental conditions exist throughout various land uses which necessitate different methods to test metal contamination based on local health risks.

Human Health Risk Assessment (HHRA) Framework

The creation of health policies from chemical speciation data requires an advanced mathematical system which serves as the essential foundation. The

Human Health Risk Assessment (HHRA) model developed by the United States Environmental Protection Agency (USEPA) serves as the primary assessment method for this process. The model divides risk assessment into two distinct categories which include non-carcinogenic hazards and carcinogenic risks. The HHRA method calculates the probability of health effects occurring in a specific group through its analysis of heavy metal levels found in different soil types and their connection to human health information.

Measuring Exposure: The Average Daily Dose (ADD)

The process of risk assessment begins with the calculation of Average Daily Dose (ADD) which measures how much heavy metal a person absorbs through their body weight each day. The three main exposure pathways are evaluated through separate calculations which include accidental soil particle ingestion (ADD_ing) and soil dust inhalation (ADD_inh) and skin absorption (ADD_der).
The standard equation for ingestion is:

$$\mathbf{ADD\_ing = (C \times IngR \times EF \times ED) / (BW \times AT) \times 10^{-6}}$$

The equation defines C as the metal concentration which should be measured as the bioavailable fraction. The equation exhibits IngR as the ingestion rate while EF measures how often people are exposed to a substance throughout the year. ED shows how many years people are exposed to a substance and BW measures the average body weight of people while AT refers to the time period used for averaging [13]. Children exhibit higher ADD values than adults because they engage in hand-to-mouth activity more frequently and they have lower body weight which makes them more vulnerable to both urban and agricultural environments.

Characterization of Non-Carcinogenic Hazards

To determine whether the expected exposure amounts create a risk for non-cancerous health effects, researchers compare Average Daily Dose (ADD) measurements against Reference Dose (RfD) standards, which establish maximum safe daily exposure limits for extended periods. This comparison is articulated through the Hazard Quotient (HQ):

$$\mathbf{HQ = ADD / RfD}$$

Anytime an individual metal's hazardous quotient exceeds 1.0, the potential exists for non-carcinogenic adverse effects to occur. The Hazard Index (HI) assessment for a site requires multiple metal exposures because people encounter multiple metals at the same time. The health risk assessment indicates hazardous conditions when metal mixtures report an HI value above 1 which links back to their combined hazardous effects. The situation occurs most frequently in urban areas which experience high pollution because lead (Pb), zinc (Zn), and copper (Cu) exist at elevated levels [14].

Estimation of Carcinogenic Risk

The risk for metals identified as human carcinogens, including arsenic (As), cadmium (Cd), and hexavalent chromium (Cr VI), is quantified as the additional likelihood of an individual developing cancer over their lifetime. This is determined by multiplying the ADD by a substance-specific slope factor (SF):

$$\mathbf{CR = ADD \times SF}$$

The Carcinogenic Risk (CR) which results from this calculation shows the estimation of cancer risk as a statistical measure. The CR value 1×10^{-6} indicates that people exposed to this risk face a one-in-a-million chance of developing cancer. Regulatory agencies often deem risks between 10^{-6} and 10^{4} as reasonable or bearable. Values over 10^{4} typically necessitate remedial actions or public health interventions [15]. The use of bioavailable chemical speciation data instead of total metal concentrations for these calculations results in improved accuracy for the computations. The method usually shows that actual health dangers are lower than what conservative models which depend only on total metal concentration predict.

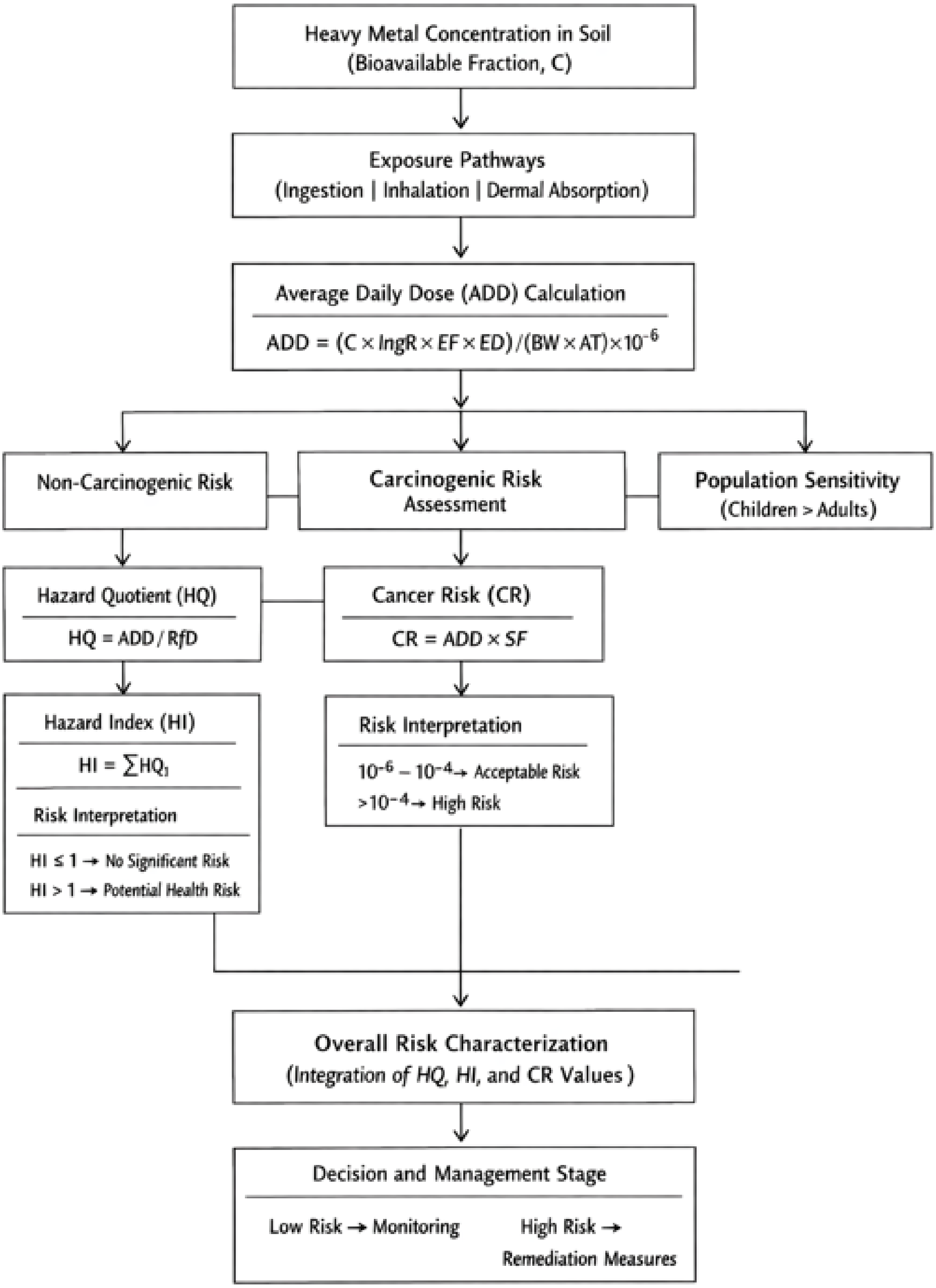

Figure 3: Human health risk assessment framework, Source: Author Generated

Heavy Metal	**Oral RfD (mg/kg/day)**	**Dermal RfD (mg/kg/day)**	**Inhalation RfD (mg/kg/day)**	**Oral Slope Factor (SF) $(mg/kg/day)^{-1}$**
Lead (Pb)	3.5×10^{-3}	5.25×10^{-4}	3.5×10^{-3}	8.5×10^{-3}
Cadmium (Cd)	1.0×10^{-3}	1.0×10^{-5}	1.0×10^{-3}	6.1
Arsenic (As)	3.0×10^{-4}	1.23×10^{-4}	3.0×10^{-4}	1.5
Chromium (Cr)	3.0×10^{-3}	6.0×10^{-5}	2.86×10^{-5}	0.5
Copper (Cu)	4.0×10^{-2}	1.2×10^{-2}	4.0×10^{-2}	N/A
Zinc (Zn)	3.0×10^{-1}	6.0×10^{-2}	3.0×10^{-1}	N/A
Nickel (Ni)	2.0×10^{-2}	5.4×10^{-3}	2.0×10^{-2}	0.84

Table 1:Reference Dose (RfD) and Slope Factor (SF) Values for Selected Heavy Metals, Source: Author Generated

Mitigation Strategies and Future Perspectives

Integrating chemical speciation data with environmental management systems provides economically viable strategies that facilitate environmental protection via targeted remediation techniques. The principal environmental concern in urban settings arises from metal-laden dust, which can be effectively controlled through the application of "physical stabilization" and "green-capping" approaches. The establishment of robust vegetation or the use of non-hazardous chemical binders mitigates the potential for contaminated topsoil to become airborne, thereby safeguarding human health from hazardous exposure. The agricultural sector predominantly employs "chemical immobilization" as its primary method for managing chemical substances [16].Biochar and zeolites and lime create soil pH improvements while providing functional groups which sequester metals into "residual" or "oxidizable" fractions. The treatments protect the food chain because they "lock" Cadmium and Lead into stable mineral phases.

The literature presents many critical gaps which remain unfilled despite advancements in analytical methods. Most health risk models ignore climate change and assume soil as a static medium. Flooding and extreme heat cycles create rapid changes in soil redox potential and organic matter decomposition. The "chemical time bomb" phenomenon occurs when variations lead to metal release from both reducible and oxidizable fractions into the exchangeable fraction. Researchers have not yet examined the "cocktail effect" which studies how heavy metals and microplastics combine to function as metal transporters through their high-surface-area characteristics. The study must observe speciation processes in two different ways first by conducting ongoing observations of their development and second by measuring their real-time transformations to protect public health.

II. Conclusion

This study shows that environmental research should move beyond its current limits of measuring "total concentration". The total loads create a base measurement for contamination assessment but chemical speciation provides actual risk information because it distinguishes between stable mineral forms and dangerous bioavailable materials. The research shows that chemical form determines risk assessment while Element presence alone does not provide adequate information. The study showed that urban road dust carries different technogenic fingerprints than the agricultural soils which show chemical contamination through pH-dependent patterns. The USEPA framework together with speciation data should be used to calculate Hazard Quotients and Carcinogenic hazards because it shows how soil chemistry affects site-specific hazards which depend on pollutant volume. The future of soil health depends on the convergence of molecular chemistry and adaptive management systems which will endure a changing global environment.

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